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4-(4-Biphenyl)-2,3,5,6-tetrafluoropyridine, a new material for application in light-emitting diodes

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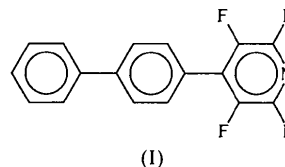
Abstract

Thin films of the title compound, C₁₇H₉F₄N, are used as electron-transport layers in organic light-emitting diodes. The molecules crystallize in a layered structure, with the aromatic planes of neighbouring molecules approximately parallel to each other. The conformation of the molecule is expressed by tilting of the pyridyl and

phenyl planes by 46.8(1) and 40.3(1)°, respectively, relative to the central benzene ring.

Comment

The title compound, (I), was synthesized for application in organic-based light-emitting diodes (LEDs). This partly fluorinated compound is a suitable material for electron-transport layers in heterostructured devices (Winkler *et al.*, 1998). LEDs are sandwich devices built from thin films of electrodes, hole- and electron-transport layers, and the electroluminescent layer (Adachi *et al.*, 1990). The electrical and optical properties of the electroluminescent layer depend strongly on the orientation and conformation of the molecules in the other layers. Therefore, knowledge of the crystal structure of the title compound is necessary for the determination of the preferred growth and orientation of the molecules within these thin films.



Single crystals of (I), synthesized and purified according to Winkler (1997), were grown from a toluene solution. Within the crystal, the molecules are packed in a layered structure. These layers are parallel to (001) and the individual molecules are arranged perpendicular to the layer. Therefore, the thickness of one layer corresponds to the length of the molecule. However, two neighbouring molecules in one layer are centrosymmetric relative to each other, which results in a reverse arrangement of the pyridyl rings, as depicted in Fig. 1. A centre of symmetry of space group $P\bar{1}$ is located in the middle of the two central benzene rings, which are therefore parallel to each other. The outer phenyl and pyridyl rings of these two neighbouring molecules are tilted 6.6(6)° relative to each other. Between these aromatic planes, the closest intermolecular distance is that between the two atoms C9 and C11ⁱ, at 3.486(2) Å [symmetry code: (i) 1 - x, 1 - y, -z]. It is probable that parallel packing of neighbouring molecules is the main interaction in the title compound, as is often observed in systems with fluorinated aromatic rings (Dahl, 1994). This parallel packing is also observed in other fluorinated aromatics, such as 2,3,5,6-tetrafluorobiphenyl (Goodhand & Hamor, 1978) and 2,3,4,5,6-pentafluorobiphenyl (Brock *et al.*, 1978), and in the biphenyl perfluorobiphenyl complex (Naae, 1979).

The inter-ring C5—C6 and C9—C12 bond lengths are 1.489(2) Å and 1.498(2) Å, respectively; these two

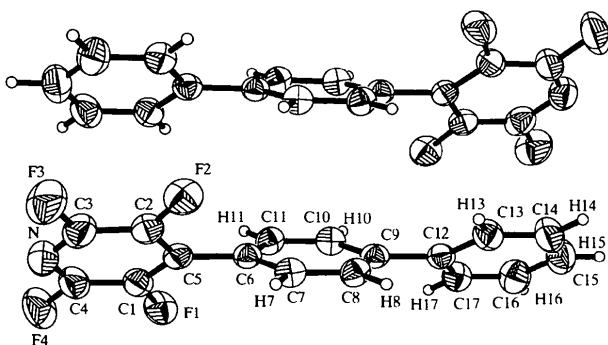


Fig. 1. Two neighbouring molecules of the title compound. The centre of symmetry is located between the two central benzene rings. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

distances are typical single-bond lengths in aromatic molecules. Within the aromatic rings, the bond lengths are around 1.39 Å. The smallest and largest inter-ring bond lengths are given in Table 1. The dihedral angle between the outer phenyl and the central benzene rings is $\varphi_1 = 40.3(1)^\circ$, while that between the central benzene and the pyridyl rings is $\varphi_2 = 46.8(1)^\circ$.

Ab initio quantum chemical calculations were performed using the software package GAUSSIAN94 (Frisch, 1995) at the HF/SVP level (Hartree–Fock method and atomic basis set of the quality Split Valence + Polarization functions) of the theory. Partial geometry optimization was carried out: dihedral angles between the outer phenyl and the central benzene rings, and between the central benzene and the pyridyl rings were optimized, while all other geometry parameters were fixed. These calculations reveal $\varphi_1 = 44^\circ$ and $\varphi_2 = 54^\circ$. At the optimized geometry, a permanent electrical dipole moment of 4.6 D along the long axis of the molecule was obtained ($1 \text{ D} \approx 3.33564 \times 10^{-30} \text{ C m}$).

Experimental

Synthesis of (I) was carried out under a nitrogen atmosphere, using biphen-4-ylboronic acid (from the Grignard reaction with 4-bromobiphenyl and further reaction with trimethylborate, resulting in the free acid after precipitation with HCl) and 4-bromo-2,3,5,6-tetrafluoropyridine in the presence of tetrakis(triphenylphosphine)palladium catalyst. Toluene was used as the solvent and an aqueous solution of 2 M K₂CO₃ was used as the base (Suzuki reaction). The mixture was stirred for 5 d at a temperature of 363 K. Five drops of H₂O₂ (35%) were added, then CH₂Cl₂ was used to dilute the system and the reaction was extracted with 1 M KOH, 1 M HCl and H₂O. The organic phase was dried with Na₂SO₄ and the solvent removed. The residue was recrystallized from toluene.

Crystal data

C₁₇H₉F₄N
M_r = 303.25

Mo *K*α radiation
 $\lambda = 0.71073 \text{ \AA}$

Triclinic

*P*1̄
a = 6.1418 (2) Å
b = 7.53250 (10) Å
c = 14.5931 (5) Å
 $\alpha = 91.876(2)^\circ$
 $\beta = 101.7100(10)^\circ$
 $\gamma = 95.106(2)^\circ$
V = 657.55 (3) Å³
Z = 2
D_x = 1.532 Mg m⁻³
D_m not measured

Cell parameters from 2011 reflections

$\theta = 1.46\text{--}26.38^\circ$
 $\mu = 0.130 \text{ mm}^{-1}$
T = 293 (2) K
 Plate
 0.66 × 0.40 × 0.03 mm
 Colourless

Data collection

Siemens CCD diffractometer
 ω scans
 Absorption correction: none
 4231 measured reflections
 2666 independent reflections
 2011 reflections with
 $I > 2\sigma(I)$

*R*_{int} = 0.026
 $\theta_{\text{max}} = 26.38^\circ$
 $h = -7 \rightarrow 7$
 $k = -6 \rightarrow 9$
 $l = -17 \rightarrow 18$

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.167$
S = 1.189
 2665 reflections
 199 parameters
 H-atom parameters
 constrained

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.039$
 $\Delta\rho_{\text{max}} = 0.200 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.321 \text{ e \AA}^{-3}$
 Extinction correction: none
 Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

F1—C1	1.350 (2)	C2—C5	1.386 (2)
F2—C2	1.350 (2)	C6—C7	1.403 (2)
F3—C3	1.331 (2)	C9—C10	1.393 (2)
F4—C4	1.340 (2)	C14—C15	1.374 (3)
N—C3	1.307 (3)	C15—C16	1.373 (3)
N—C4	1.305 (3)	C5—C6	1.489 (2)
C1—C4	1.378 (3)	C9—C12	1.498 (2)
C4—N—C3	116.7 (2)	C2—C5—C1	114.5 (2)
N—C4—C1	124.2 (2)	C10—C9—C8	117.9 (2)
C4—C1—C5	120.3 (2)	C13—C12—C17	118.5 (2)
C8—C9—C12—C13	−40.5 (2)	C1—C5—C6—C7	46.4 (2)
C10—C9—C12—C17	−39.9 (2)		47.0 (2)

Data were collected using ω scans of 0.03° . 1250 frames with 20 s measuring time covered about one hemisphere of data. All non-H atoms were refined anisotropically. The H atoms were located at the expected positions and refined with the riding model in three groups with different isotropic coefficients, where the atoms were assigned according to increasing distance from the central ring.

Data collection: XSCANS (Siemens, 1996b). Cell refinement: SMART (Siemens, 1996a). Data reduction: SAINT (Siemens, 1996a). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL (Siemens, 1995). Software used to prepare material for publication: SHELXTL.

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Ethylenebis(phosphonic acid)

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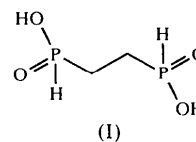
Abstract

The as yet structurally uncharacterized title compound, $C_2H_8O_4P_2$, was isolated as a by-product of the synthesis of 1,2-bis(dimethylphosphino)ethane (dmpe) from 1,2-

bis(dichlorophosphino)ethane. In the crystal structure, which is characterized by strong intermolecular $O—H \cdots O$ hydrogen bonds, only the R^*,S^* diastereomer is found. The molecule is located on a center of inversion intersecting the central C—C bond, thereby preserving the molecular C_i symmetry.

Comment

Phosphonic acid is known to form strong hydrogen bonds which result in enhanced viscosity with increasing concentration. In molecular crystals, hydrogen bonds are among the most important structure-determining interactions. The structure of methylenebis(phosphonic acid) (King *et al.*, 1996) is characterized by intermolecular hydrogen-bonded molecules, as is the structure of ethylenebis(phosphonic acid), (I), reported here.



In the monoclinic unit cell, the central C—C bond of ethylenebis(phosphonic acid) is located at a center of inversion and, as a result, only one-half of a symmetrically independent molecule needs to be discussed. The geometry at the P atom is very similar to that found in methylenebis(phosphonic acid), which has two independent P atoms in the asymmetric unit. Due to the presence of electron-withdrawing O atoms at the P atom, the P—C bond is shortened to 1.784 (2) Å. All H atoms have been located. An H atom is located at only one of the O atoms, and the mesomeric structure proposed for the liquid state is not present in the solid. The intermolecular distance between O atoms involved in hydrogen bonding is 2.511 (3) Å [O2—H2 0.94 (4), H2...O1ⁱⁱ 1.58 (4) Å and O2—H2...O1ⁱⁱ 171 (4)°; symmetry code: (ii) $\frac{1}{2} + x, \frac{3}{2} - y, z - \frac{1}{2}$]. This affords a co-operative chain of $\cdots O=P—OH \cdots$ hydrogen bonds linking both ends

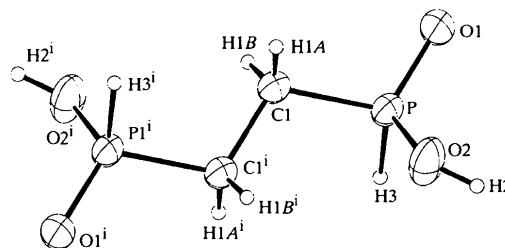


Fig. 1. View of the title compound with displacement ellipsoids at the 50% probability level. H atoms are shown as circles of an arbitrary radius. [Symmetry code: (i) $-x, 1 - y, 1 - z$]